

# Foreword

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The most important change in the arsenal of computational tools of molecular quantum chemistry in this decade is the rise of density functional theory (DFT) from a little appreciated method that was not readily accepted in the community to a highly valuable technique that has become competitive with the best conventional *ab initio* methods. The introduction of gradient-corrected (nonlocal) functionals quickly led to the development of new mathematical expressions for exchange and correlation terms, which impressed scientists by the accuracy of the calculated geometries, energies, vibrational frequencies, NMR chemical shifts, and other important molecular properties. Within a relatively short period of time, new abbreviations such as B3LYP, BP86, KS orbitals, etc., became as ubiquitous in publications of computational chemistry as HF, MP2, and CCSD(T). It is amazing how fast results of DFT calculations were routinely reported in theoretical reports, after it was recognized in comparative studies that the new DFT methods gave equal or even better results at lower computational costs than classical *ab initio* techniques. At present it seems that gradient-corrected DFT is on its way to replacing conventional *ab initio* methods as the standard technique for calculating medium-sized molecules.

In retrospect, it is amusing to see the initial resistance of theoretical chemists—including the writer of this foreword—against using DFT. It seemed to be clear that further development of accurate theoretical methods should be expected from the established paradigm of Hartree–Fock plus correlation treatment. Suddenly, there was a

profound change in theory, and the establishment was skeptical of newcomers who claimed that they could do calculations better and cheaper. The resistance was soon overcome when the advantages of nonlocal DFT methods became obvious. DFT is now accepted as a very important addition to the set of theoretical methods for calculating molecules. However, in spite of the impressive success of DFT in recent years, pioneers of DFT still call it “an immature subject.”<sup>1</sup> This means that more progress can be expected from the youngest member of established computational chemistry methods.

DFT came as a lucky chance to theoretical chemistry in aspects other than simply giving accurate numbers at low costs. It has been shown that the Kohn–Sham (KS) orbitals, which were originally introduced only as a means to calculate electron densities, are very similar to conventional HF orbitals. HF orbitals are used as a conceptual framework for the qualitative interpretation of molecular structure and reactivity, and chemical models like the frontier orbital theory have become very important not only in theoretical chemistry but also in general chemistry. The similarity of KS and HF orbitals means that MO-based chemical models can also be used when DFT calculations are carried out. Because HF orbitals do not include correlation effects, and KS orbitals do, the latter should be even better models for chemical concepts. Another fortunate finding was that effective core potentials, which were developed for conventional *ab initio* methods, can also be used for DFT calculations.

Because the *Journal of Computational Chemistry* focuses on progress in the field of theoretical chemistry methods, the editors found it appropriate to devote a special issue to DFT. We did not want to publish another set of review articles, because they are available from several books that have been published in the recent past. Rather, we were trying to collect articles that indicate the present state of the art and possible future directions of DFT. I thank all authors who contributed a manuscript to this special issue.

*Note Added in Proof.* The timelines of the topic has spectacularly been confirmed by awarding the 1998 Nobel prize in chemistry equally to John Pople for his development of computational methods in quantum chemistry, and to Walter Kohn for his development of the density functional theory.

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## Reference

1. Parr, R. G. *Top Curr Chem* 1996, 180, vii.